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Amperometric-type NOx sensor based on YSZ electrolyte and La-based perovskite-type oxide sensing electrode

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At present, lean-burn type engines or diesel engines for passenger cars have been developed and installed into automobiles to improve fuel efficiency. In these cases, NOx storage catalysts or selective catalytic reduction (SCR) systems are also installed for reducing NOx emission. In order to control these systems more efficiently, NOx sensor which responds selectively, quickly, and quantitatively are necessary. Here we focused on the NO direct decomposition function of La-based perovskite oxides. We applied them to a sensing electrode for the amperometric NOx sensor using yttria-stabilized zirconia (YSZ). $La_{0.8}Sr_{0.2}MO_3$ (M = Co, Mn, Fe, Ni) powders were synthesized by means of spray pyrolysis method. Among four kinds of oxides studied, the sensor using $La_{0.8}Sr_{0.2}MnO_3$–SE showed the highest sensitivity to NO_2 as well as low base current even in the presence of excess O_2 (21 vol%). The sensor also exhibited excellent NO_2 selectivity at 500°C. The sensitivity was increased with an increase of NO_2 concentration in an examined range between 50 to 800 ppm, and did not change in the examined O_2 concentration range (5–21 vol%).

Key-words : Gas sensor, NOx, Amperometric, YSZ, Perovskite, Spray pyrolysis

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1. Introduction

In these days, decreasing the amount of CO_2 emission from automobile industry is strongly required to prevent global warming. Therefore, new-type engines such as lean-burn type engines or diesel engines for passenger cars have been developed in order to improve fuel consumption. On the other hand, the treatment of NOx emitted from these engines has become problems, because conventional treatment system (three way catalyst) does not work properly under lean-burn (air rich) condition. Thus, new-treatment systems such as NOx storage catalysts or selective catalytic reduction (SCR) systems were developed. In these systems, appropriate amount of injection of gasoline or urea as a reduction component, respectively, are necessary. Therefore, in order to control these amounts, there is a strong demand for NOx sensor which responds selectively, quickly, and quantitatively.

In regard to NOx sensor, zirconia-based type has possibilities in practical application because of mechanical and chemical stability of YSZ even at high temperature. In fact, amperometric-type NOx sensor went on the market early in the 2000 s.[1] The sensor mainly consists of two chambers. In the first chamber, oxygen concentration is controlled at a constant value, and NO_2 is converted into NO. In the second one, NO is decomposed into N_2 and O_2, O_2 concentration is measured by limiting-current type oxygen sensor. Extracting O_2 from exhaust gas seems to be difficult and costly because sensor signal is largely influenced by O_2 concentration. In addition, mixed-potential type NO_2 sensors have been studied and reported.[2)–11)] These sensors consist of electrolyte, sensing electrode (SE), and reference electrode (RE). The anodic reaction of O_2 and the cathodic reaction of NO_2 proceed simultaneously at the SE/YSZ interface. When the rate of the anodic reaction is equal to that of the cathodic reaction, the mixed potential arises at SE. Several materials such as NiO, WO_3 $La_{0.8}Sr_{0.2}CrO_3$ were reported as promising materials for detection of NOx. However, O_2 is involved in total reactions. There is a possibility that sensor signal is influenced by the change of O_2 concentration. Therefore, direct reaction of NOx should be taken as a sensor signal for preferential detection of NOx even in the excess O_2 condition.

We have focused on the property of La-based perovskite oxides to decompose NO into O_2 and N_2. The NO decomposition function on these oxides was reported as follows.[12)–15)] At first, the NO molecule adsorbed on the adjacent oxide ion vacancies. The second NO adsorbed on the oxide ion vacancies, and then N_2 was released into gas phase. Finally, O_2 was released into gas phase. We tried to apply this material for the YSZ-based gas sensor. We used this oxide as a sensing electrode and assembled a sensor element using YSZ as an electrolyte. In order to utilize this decomposition function for NOx detection, we applied the potential between SE and counter electrode (CE) for the sensor in NOx condition. We expected the remained oxygen on the oxide vacancy was ionized instead of releasing into gas phase, and O^{2-} moved to the counter electrode. Direct current flowed in the circuit of the sensor at the same time, and its value was used for a sensor signal. In this case, if O^{2-} derived from NOx is much higher than the one from O_2, we can detect NOx even in the excess O_2 condition. Until now, we have reported the YSZ-based amperometric NOx sensor attached with $La_{0.6}Sr_{0.4}Co_{0.98}Mn_{0.02}O_3$–SE showed high sensitivity and selectivity to NOx.[16),17)] According to several reports, the valence variation of transition metal in La-based perovskite plays an important role for decomposition of NO into O_2 and N_2.[14),15)] In this paper, La-based perovskite oxides, $La_{0.8}Sr_{0.2}MO_3$ (M = Co, Mn, Fe, Ni) powders were synthesized by spray pyrolysis method and the sensing performance as amperometric NOx sensor were examined.

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2. Experimental

2.1 Preparation of materials

The perovskite oxides were prepared by spray pyrolysis method. The precursor solutions were made from $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd.), $Sr(NO_3)_2$ (98%, Kanto Chemical Co., Inc.) and each of $Co(NO_3)_2 \cdot 6H_2O$ (99.5%, Wako Pure Chemical Industries, Ltd.), $Mn(NO_3)_2 \cdot 6H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd.), $Fe(NO_3)_3 \cdot 9H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd.), $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Wako Pure Chemical Industries, Ltd.). Each of these solutions was misted ultrasonically and introduced to the tubular furnace kept at 800°C with air flowing, which was subsequently calcined at 800°C for 2 h in air. The obtained products were characterized by X-ray diffractometry (XRD, RINT 2000, Rigaku Denki Co., Ltd.) using Cu Kα radiation and scanning electron microscopy (SEM, S–4500, Hitach High-Technologies Co.).

2.2 Measurement of sensing properties

The each of obtained powders was thoroughly mixed with α-terpineol in the weight ratio of 1:1 and screen-printed on one side of YSZ pellet (ϕ = 9 mm, t = 1.5 mm) as a SE. In addition, the pure Pt paste was also screen-printed on the other side of YSZ pellet to form a counter electrode (CE). The fabricated sensor element was attached to magnesia tube with inorganic adhesive as shown in **Fig. 1**.

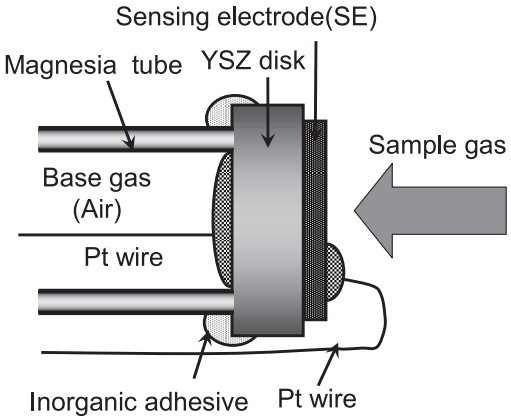

Fig. 1. Schematic view of YSZ-based sensor using the perovskite oxide-SE.

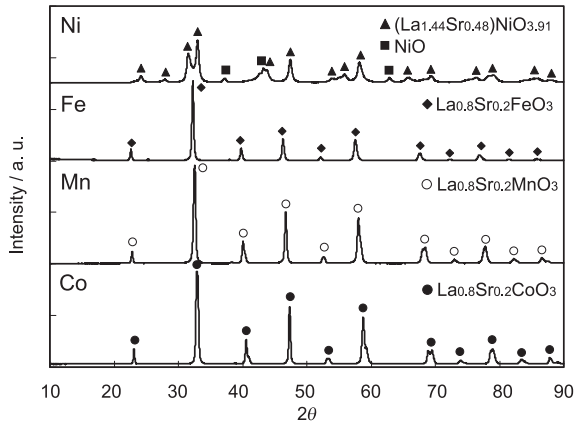

Fig. 2. XRD patterns of the La-based oxide powders prepared by spray pyrolysis.

The fabricated sensor was assembled in a quartz tube and the sensing characteristics were measured using a conventional gas-flow apparatus equipped with a furnace operating in the temperature range of 400–650°C. The total flow rate of the base gas (dry synthetic air) or the sample gas was fixed at 100 cm^3/min. The sample gases were prepared by diluting the parent gases with dry synthetic air. Reaction curves of the sensor were measured using a potentiostat (Solartron–1287, Solartron, UK). The current–voltage (polarization) curves were measured at a scan rate of 12 mV/min using two-electrode setup. The complex impedance measurements were performed by means of complex impedance analyzer (Solartron–1287, Solartron, UK) in the frequency range of 0.1 Hz–0.1 MHz and a.c. amplitude was kept at 10 mV.

3. Results and discussion

3.1 Characterization of synthesized oxides

In this paper, four kinds of transition metal, Co, Mn, Fe, Ni, were focused on the constituent elements of La-based perovskite, and 20 mol% La was replaced for Sr to increase oxide ion vacancies as a reaction site of NOx in the perovskite structure. **Figure 2** shows XRD diffraction patterns of La-based perovskite oxides ($La_{0.8}Sr_{0.2}MO_3$, M = Co, Mn, Fe, Ni). The each of oxides which contains Co, Mn, and Fe was characterized as a perovskite structure, namely, $La_{0.8}Sr_{0.2}CoO_3$ (LSC), $La_{0.8}Sr_{0.2}MnO_3$ (LSM), $La_{0.8}Sr_{0.2}FeO_3$ (LSF), respectively. On the other hand, the diffraction pattern containing Ni was mainly recognized as $(La_{1.44}Sr_{0.48})NiO_{3.91}$ and NiO. Although the composition was different from perovskite, the performance as a sensing-electrode material for the sensor was performed. Hereafter, it was abbreviated to LSN. **Figure 3** shows the SEM images of these oxides. Grain's shape of oxides except in the LSC was sphere, while the LSC powder has irregular surfaces. All of oxides had various grain size ca 0.3–1 μm.

3.2 Characteristics of synthesized oxides as a sensing electrode for the sensor

In order to examine the property of the sensing electrode, polarization curve measurements of the sensor attached with four kinds of oxides were performed in base air, NO (500 ppm), and NO_2 (500 ppm) at 600°C. The cathodic current in all gases was

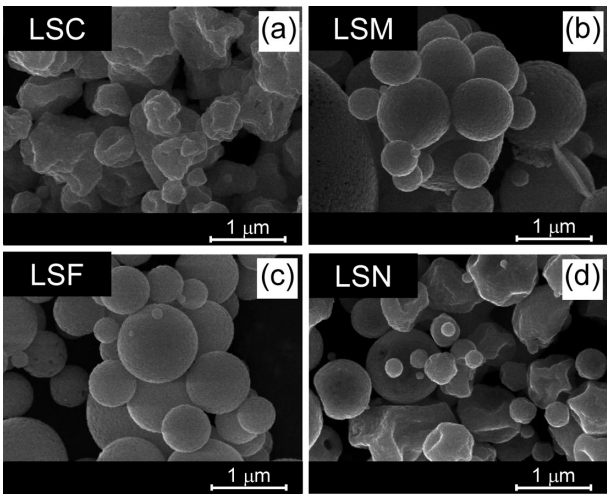

Fig. 3. SEM images of the obtained oxide powders by spray pyrolysis (a) LSC, (b) LSM, (c) LSF, (d) LSN.

increased with increasing the cathodic potential and their current both in NO and NO_2 was larger than the base current in all sensors. In addition, the increment of this current in the NO_2 was larger than the one in the NO in the examined range. This tendency was similar to previous results.[16] Generally, automobile exhaust contains both NO and NO_2, and it is possible to convert NO into NO_2 by using oxidation unit. Thus, NO_2 was chosen as a representative of NOx to obtain a better sensing signal. **Figure 4** shows the comparison of the current values to base gas and 500 ppm NO_2 of the sensor using the four kinds of oxide-SE at applied potential of –50 mV (vs. Pt–CE) as well as the occupancy of NO_2 sensitivity ($I_{NO_2} - I_{base}$) in total current (I_{NO_2}) as a rhombus shape. In this figure, LSM–SE and LSF–SE showed the high sensitivity to NO_2, and LSM–SE showed lower base current than LSF–SE. LSM–SE also showed the highest occupancy rate of NO_2 sensitivity in total current. These facts mean the sensor using LSM–SE has a possibility detecting low concentration of NO_2 even in the excess of O_2. Thus, LSM was chosen as the appropriate material in this study. The mechanism which LSM showed the optimum response to NO_2 and O_2 is under consideration.

One of advantages of amperometric type gas sensors is the improvement of selectivity in coexisting gases with optimization of the applying potential.[18)–20)] **Figure 5** shows the polarization curves of the sensor attached with LSM–SE in the range of 0 – –100 mV (vs. Pt–CE) in the base gas and the each of sample gases (NO, CO, C_3H_6, NH_3, 500 ppm each) operated at 600°C.

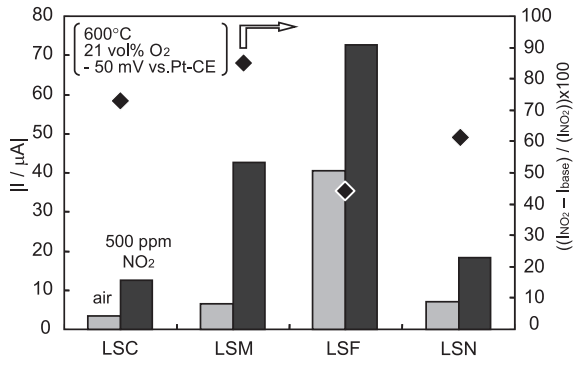

Fig. 4. Comparison of response current to base gas and 500 ppm NO_2 as well as the occupancy of NO_2 sensitivity in total (◆) of the sensor using La-based perovskite oxides at 600°C.

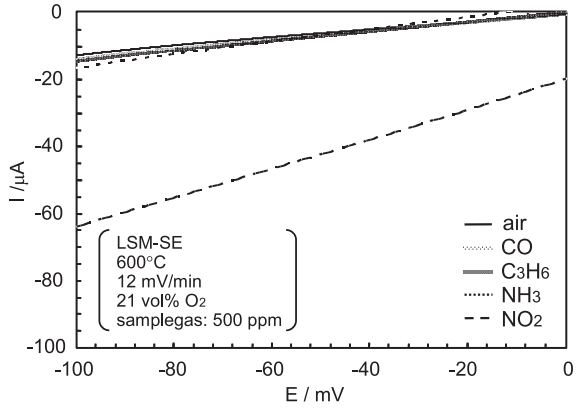

Fig. 5. Polarization curves obtained in base gas and various gases (CO, C_3H_6, NH_3, NO_2: 500 ppm) in the potential range of 0 to –100 mV (vs. Pt–CE) for the sensor attached with LSM–SE at 600°C.

It is turned out that cathodic current in the NO_2 was larger than the value in the base gas in the examined range. The obtained curves in each of CO and C_3H_6 were almost same with the results in the base gas. In the case of NH_3, the shape of the curve was a slight difference with the results in the base gas. Although the cathodic current was lower than the base current at applied potential 0 mV(vs. Pt–CE), the current value was increased with increasing applied potential and caught up with the value obtained in the base gas and exceeded eventually. Thus, the best applied potential which shows the finest selectivity of the sensor to NO_2 was found to be –50 mV.

Here, in order to understand the reaction on the LSM–SE surface of the sensor, the complex impedance measurement was examined in the base gas and the various sample gases. The results summarizes in **Fig. 6**. The obtained spectrum in the base gas was divided into two semicircles and the one which measured at lower frequency range was larger. When the gas flow was switched from the base gas to NO_2, the shrinkage of larger semicircle was observed. The size of semicircle obtained in CO was almost same with the one in base gas. While the semicircles was shrinked the kind of gas was changed from base gas to C_3H_6 or NH_3, the each of diameter of semicircles were still large in comparison with the results obtained in NO_2. The diameter of the semicircle has interpreted as the resistance of the electrode reaction.[21] Considering the complex impedance measurement and

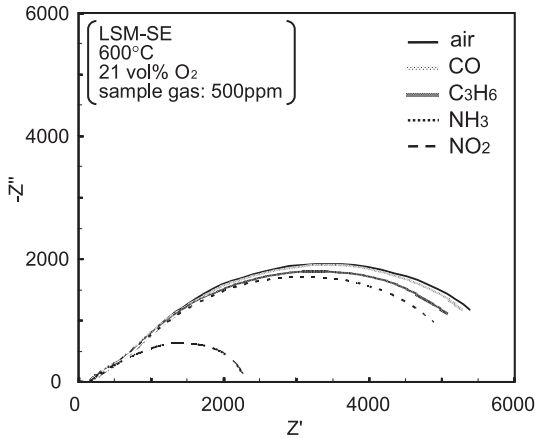

Fig. 6. Nyquist plots in base gas and various gases (NO_2, CO, C_3H_6, NH_3: 500 ppm) with the potential of open circuit voltage (vs. Pt–CE) for the sensor attached with LSM–SE at 600°C.

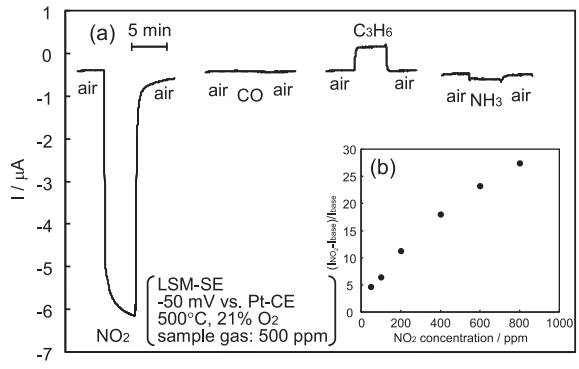

Fig. 7. (a) Response transient to various gases (NO_2, CO, C_3H_6, NH_3: 500 ppm), (b) dependence of sensitivity on the NO_2 concentrations for the sensor attached with LSM–SE at 500°C.

NO decomposition mechanism of La-based perovskite oxide, a sequence of reaction, namely, the preferential adsorption of NO_2, decomposition into NO and/or N_2, and reduction of remained O into O^{2-} on the oxygen vacancies, seems to be proceeded. However, the details of reaction mechanism are under investigation.

To choose optimum operation temperature, the current responses of the sensor to base gas and the 500 ppm NO_2 were measured at 400, 450, 500, 550, 600, 650°C. Although the sensitivity was the lowest to NO_2 at 400°C, the high occupancy rate of NO_2 sensitivity in total current was observed. Increasing the operating temperature, the ratio of NO_2 sensitivity in total was decreased and sensitivity to NO_2 was increased. Thus, considering these two factors, the optimum operation temperature was considered to be 500°C.

Figure 7(a) shows response transients to NO_2, CO, C_3H_6, NH_3 (500 ppm each) of the sensor using LSM–SE at –50 mV (vs. Pt–CE) at 500°C. It is seen that the base current was low and the current response to NO_2 was high. The sensitivity to 500 ppm NO_2 was about 6 μA and 90% response and recovery rates were less than 40 s. The sensor did not respond to CO. Although the sensor slightly responded to NH_3 and C_3H_6, the sensitivities of these gases were much lower than the NO_2. Figure 7(b) depicts the degree of the sensitivity divided by the base current ($|I_{NO_2} - I_{base}| / |I_{base}|$) on the concentration of NO_2 in order to evaluate quantitative performance of the sensor. The response increased with increasing the concentration of NO_2 between 50–800 ppm, and the sensitivity to 50 ppm NO_2 of the sensor was more than four times higher than the base current.

It is necessary the sensor showed stable response to NO_2 in the wide range of O_2 concentration. **Figure 8** summarizes the current value to 500 ppm NO_2 and base current with the change of O_2 concentration (5–21 vol%) of the sensor attached with LSM–SE at 500°C. The current value in base gas was almost same in the examined range of O_2 concentration. Though the current values in the 500 ppm NO_2 decreased slightly with the increase of the O_2 concentration, the presented sensor showed almost same sensitivity to 500 ppm NO_2.

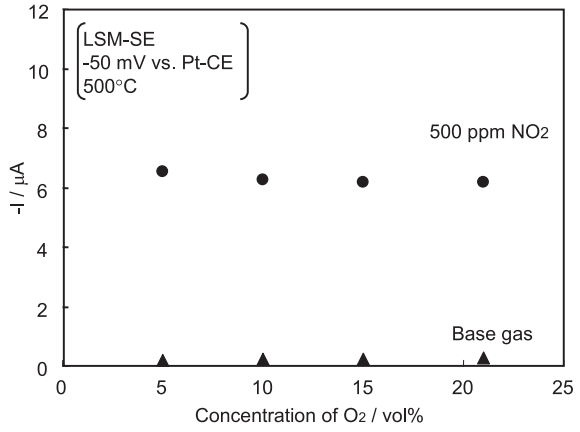

Fig. 8. Dependence of current response to base gas and 500 ppm NO_2 in the concentration range of O_2 (5–21 vol%) for the sensor attached with LSM–SE at 500°C, aplied potential: –50 mV vs. Pt–CE.

4. Conclusions

Four kinds of La-based perovskite-type oxides, $La_{0.8}Sr_{0.2}MO_3$ (M = Co, Mn, Fe, Ni) were synthesized by spray pyrolysis method, and sensing properties of zirconia-based amperometric-type sensor using the oxides as sensing electrode (SE) were examined. The obtained oxides containing each of Co, Mn, and Fe were characterized as a perovskite. The sensor attached with $La_{0.8}Sr_{0.2}MnO_3$ showed the highest sensitivity to NO_2 as well as selective response. The sensitivity was increased with increasing the concentration of NO_2 in the examined range of 50 – 800 ppm. The sensitivity to NO_2 wasn't almost influenced by the change of the O_2 concentration between 5–21 vol%.

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